

MODERN OXIDE MATERIALS

Preparation, Properties and Device Applications

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formed. Both the non-polar high temperature and polar phases can be either orthorhombic and/or tetragonal. It is the single crystal form of the tungsten bronze type ferroelectric compounds which has been primarily studied for both ferroelectric and electro-optic properties.

The first compound of this crystal class reported to be ferroelectric was lead metaniobate, $\text{Pb}_5\text{Nb}_{10}\text{O}_{30}$ (Goodman, 1953), with both orthorhombic a and b axes polar, an exception to the rule for these compounds. Lead metaniobate has a high Curie temperature, 843°K, and was developed as a piezoelectric ceramic for use over a wide temperature range. It is an unusual material with low permittivity, moderate piezoelectric activity and very low mechanical Q. This last point is a serious drawback for many applications but is of considerable use in ultrasonic flow detection where it helps to suppress the phenomenon known as ringing.

A number of solid solutions of lead metaniobate have been studied in the polycrystalline ceramic form but the only one of any practical significance is $(\text{Pb}_{5-x}\text{Ba}_x)\text{Nb}_{10}\text{O}_{30}$. The optimum piezoelectric properties are found near a phase boundary occurring at $x = 2$, which separates two ferroelectric orthorhombic phases. Subbarao (1960) found that for $x < 2$ the polarisation was in the $\langle 110 \rangle$ direction whilst for $5 > x > 2$ the polarisation was parallel to the $\langle 001 \rangle$ direction indicating marked influence of the highly polarisable lead ion on the polar axis. Compositions around the phase boundary possess a relatively low temperature coefficient of the resonance frequency, high mechanical Q and moderately strong piezoelectric activity which renders them suitable for resonant piezoelectric devices requiring frequency stability with temperature.

Ferroelectric Ceramic Oxides

More complex compounds exhibiting the tungsten bronze structure were reported by Roth and Fang (1960), Ainger et al. (1970) and Isupov (1964). One of the more interesting compounds, barium gadolinium iron niobate, $\text{Ba}_4\text{Gd}_2\text{Fe}_2\text{Nb}_8\text{O}_{30}$, was reported to be a ferroelectric and ferromagnetic ceramic, but investigations with similar ceramics showed that the weak magnetic properties were due to the presence of a second phase, barium hexaferrite.

C. LAYER STRUCTURE OXIDES AND COMPLEX COMPOUNDS

A large number of layer structure compounds of general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{x-1}\text{B}_0\text{O}_{3x+1})^{2-}$ have been reported (Smolenskii et al. 1961; Subbarao, 1962), where $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, \text{etc.}$, $\text{B} = \text{Ti}, \text{Nb}, \text{Ta}$ and $x = 2, 3, 4$ or 5 . The structure had been previously investigated by Aurivillius (1949) who described them in terms of alternate $(\text{Bi}_2\text{O}_2)^{2+}$ layers and perovskite layers of oxygen octahedra. Few have been found to be ferroelectric and include $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ($T_c = 583^\circ\text{K}$), $\text{PbBi}_2\text{Ta}_2\text{O}_9$ ($T_c = 703^\circ\text{K}$), $\text{BiBi}_3\text{Ti}_2\text{TiO}_{12}$ or $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($T_c = 948^\circ\text{K}$), $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ($T_c = 598^\circ\text{K}$) and $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ($T_c = 583^\circ\text{K}$). Only bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has been investigated in detail in the single crystal form and is finding applications in optical stores (Cummins, 1967) because of its unique ferroelectric-optical switching properties. The ceramics of other members have some interest because of their dielectric properties.

More complex compounds and solid solutions are realisable in these layer structure oxides but none have significant practical application.

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